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A. Pappová, St. Varga, J. Noga, I. Cernusák

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MBPT AND DFT STUDIES OF HYDROGEN CYANIDE BORANE(1) OLIGOMERS, POLYMERS AND THEIR DEHYDROGENATED ANALOGS

Adriana PAPPOVÁ¤, Stefan VARGA¤, Jozef NOGA¤ and Ivan CERNUSÁK§

¤Department of Theoretical Chemistry, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84236 Bratislava,

§Department of Physical Chemistry, Faculty of Natural Science, Comenius University, Mlynská dolina, SK-84215 Bratislava

The idea of hydrogen cyanide borane(1) polymer is closely related to our previous calculations[1] of the formation of the dimer $(HCNBH)_2$. The open-chain planar E-isomer of $(HCNBH)_2$ exhibits remarkable thermodynamic stability and can be considered as the starting point for the modeling of the polymer (Fig.1). We also propose the model with two-coordinate boron (Fig.2).

Geometry optimizations and fragmentation energies of the series of oligomers based on these two structural models are performed with the aim to find the suitable reference cell of polymers for a finite-periodic-cluster (FPC) calculations of band gaps.[2] Geometry of the oligomers is examined at different computational levels: MBPT(2) (second-order Many-Body Perturbation Theory), SDQ-MBPT(4) (fourth-order Many-Body Perturbation Theory limited to singly-, doubly- and quadruply excited configurations) and DFT-B3LYP (Density Functional Theory with Becke's three parameter hybrid functional using the LYP correlation functional). Both models seem to be suitable for the polymer chain construction, because of their periodic structure emerging from successive HCNBH or HCNB addition. The stability of the oligomers (up to pentamers) with respect to the decomposition to various fragments is fairly high ranging from 111 to 441 kJ/mol for the HCNBH series and from 345 to 606 kJ/mol for the HCNB series. These fragmentation energies are related to the rupture of the weakest bonds (based on the bond order analysis).

One can consider our two polymer models as the derivatives of polyacetylene (which is widely studied for its interesting properties) and anticipate the impact of electron-donor and electron-acceptor parts in the potential polymer chain to its band structure, and hence to its possible electrical conductivity.[3,4] The band gap for our HCNB model polymer is 2.6 eV, which is smaller than the band gap for polyacetylene calculated by the use of the same level of theory: 3.8 eV.

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Fig.1

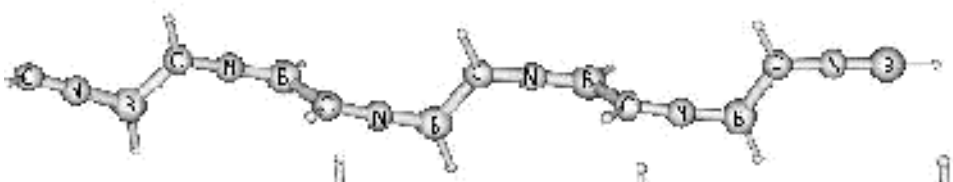

Fig.2